

$\delta^{13}\text{C}$ Analysis of Individual Compounds via GC-IRMS

1. Introduction

The determination of the $^{13}\text{C}/^{12}\text{C}$ ratio on components of individual compounds has been widely used in petroleum geochemistry for correlational analysis (e.g., Schoell et al, 1992) and paleo and modern environmental geochemistry (e.g., Hayes et al, 1990). Analyses can be performed on any GC-amenable compounds, including but not limited to natural gas components, gas condensates, oil compound classes (saturates, aromatics, etc), and biomarkers. In order to provide timely, accurate and precise carbon isotopic analyses, we utilize the latest continuous-flow technology to link a gas chromatograph to a modern isotope ratio mass spectrometer via an oxidative interface. All stable isotope methods employed by the Energy Geochemistry Laboratory follow the best practices and procedures as detailed in peer-reviewed literature.

2. Interfaces with Other Methods

None required.

3. Materials and Equipment

As described below in the Procedure.

4. Procedure

The $^{13}\text{C}/^{12}\text{C}$ ratio of GC-amenable individual compounds is determined using methods modeled after Baylis et al (1994). Analyses can be performed on any GC-amenable compounds. For example, the saturate fraction from an oil of interest is diluted in cyclohexane and injected into a HP¹ 6890 gas chromatograph (manually or via an autosampler). Individual saturate compounds are chromatographically separated on a 100% polydimethylsiloxane column (100 m x 0.25 mm x 0.5 μm). Typical GC conditions are as follows: He carrier gas @ 1.5 ml/min; 40 °C initial

¹ Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

temp; hold for 5 min; ramp to 320 °C at 5 °C/min; hold for 30 min. The individual components are then combusted in the He-1% O₂ stream at 1050 °C in an in-line Alsint-99.7 ceramic reactor (0.5 mm I.D. x 6 mm O.D. x 500 mm length, containing Ni and Pt wires as a combustion catalyst). The resulting combustion products (primarily CO₂ and H₂O) are passed through an in-line Nafion drier, and the final analyte CO₂ is passively drawn via open split into the source of a ThermoFisher MAT 253 isotope ratio mass spectrometer for subsequent carbon isotope analysis.

5. Calibration and Quality Control Samples

Carbon isotope values from the instrument undergo off-line isotope corrections for drift (¹³C vs ΔT, as runs take several hours to complete), and for isotopic linearity due to any systematic error during injection, chromatographic and oxidation processes (¹³C vs amount), and finally are normalized on the PDB (Pee Dee Belemnite) (after Paul et al, 2007). Working standards may be external or co-injected internal standards, depending on the nature of the sample to be analyzed. The final carbon isotope values represent the average of multiple replicate analyses (generally, n=3) with a standard deviation of generally better than 0.2 per mil. The accuracy of stable isotope measurements historically is not specified, neither by commercial laboratories nor instrument manufacturers. That said, as we utilize two-point calibrations, our estimated accuracy is 2 times our precision, or ± 0.4 ‰. All final δ¹³C values are reported relative to the international standard, Pee Dee Belemnite Carbonate (PDB).

6. Limits, Precautions, and Interferences

Sample requirements are as such: purified fraction of the sample compound of interest. Generally, the “cleaner” the sample injected, the closer to baseline resolution can be achieved, resulting in a more accurate/more precise carbon isotope determination.

7. Acceptance of Data

Data are deemed acceptable if working isotopic standards are within acceptable parameters (peak response, area or height, and isotopic value). Replicate analyses are usually better than 0.2 ‰ standard deviation.

8. Data Handling and Transfer

The following data are returned to the submitter: Sample ID, $\delta^{13}\text{C}_{(\text{PDB})}$, std, n; where Sample ID is the sample descriptor provided by the submitter, $\delta^{13}\text{C}_{(\text{PDB})}$ is the average carbon isotope value for the sample component, std is the standard deviation of replicate analyses and n is the number of replicate analyses. An example of a final results data table is shown below.

Sample ID	component	$\delta^{13}\text{C}_{(\text{PDB})}$ ‰	stdev ‰	n
Pionce #24H	nC10	-30.38	0.10	3
“	nC17	-28.24	0.08	3
“	pristane	-25.65	0.12	3
“	nC18	-27.57	0.15	3
“	phytane	-25.73	0.10	3
“	nC20	-28.12	0.14	3
“	nC25	-27.91	0.08	3
“	nC30	-28.00	0.05	3

Currently, with the exception of natural gases, compound specific isotope data are not submitted to the Organic Geochemistry Database.

9. References

Baylis, S.A., Hall, K., and Jumeau, E.J., 1994, The analysis of the C₁-C₅ components of natural gas samples using gas chromatography-combustion-isotope ratio mass spectrometry: *Organic Geochemistry*, v. 21, no. 6/7, p. 777-785.

Hayes, J.M., Freeman, K.H., Popp, B.N., and Hoham, C.H., 1990, Compound-specific isotope analysis: A novel tool for reconstruction of ancient biogeochemical processes: *Organic Geochemistry*, v. 16, no. 4/6, p. 1115-1128.

Paul D., Skrzypek G. and Forizs, I., 2007 Normalization of measured stable isotopic compositions to isotope reference scales – a review. *Rapid Communications in Mass Spectrometry*, v. 21, p.3006-3014.

Schoell, M., McCaffery, M.A., Fago, F.J., and Moldowan, J.M., 1992, Carbon isotopic compositions of 28,30-bisnorhopanes and other biological markers in a Monterey crude oil: *Geochimica et Cosmochimica Acta*, v. 56, no. 3, p. 1391-1399.

10. Attachments

None.

11. History of Changes

R0: Initial Issue